SQUEEZING OF A CONCENTRATED EMULSION WITH SURFACTANT THROUGH A PERIODIC POROUS MEDIUM

Alexander Z. Zinchenko, Jacob R. Gissinger and Robert H. Davis

Department of Chemical and Biological Engineering University of Colorado, Boulder, CO 80309-0424, USA

ABSTRACT

This study seeks to explore, through rigorous and accurate hydrodynamical simulations, the fundamental effects of surface contamination by surfactants on emulsion flow of deformable drops through a porous medium. As a prototype problem, high-resolution, long-time 3D simulations are presented for slow, pressure-driven flow of a periodic emulsion of deformable drops through a dense, simple cubic array of solid spheres (one drop and one particle per periodic cell). The drops, covered with insoluble, non-diffusive surfactant, are large compared to pores, and they squeeze with high resistance, very closely coating the solids to overcome surface tension and lubrication effects. The solid volume fraction is 50%, the emulsion concentration c_{em} in the pore space is 36% or 50%, the drop-to-medium viscosity ratio λ is 0.25 to 4. The contamination measure $\beta = RT\Gamma_{eq} / \sigma_0 \le 0.1$ (with the universal gas constant R, absolute temperature T, equilibrium surfactant concentration Γ_{eq} and the clean surface tension σ_0) keeps the linear surfactant model (assumed in most of the work) physically relevant. The boundary-integral solution requires extreme resolutions (tens of thousands of boundary elements per surface) achieved by multipole acceleration with special desingularizations, combined with flow-biased surfactant transport algorithms¹ for numerical stability. The time-periodic regime is typically attained after a few squeezing cycles; the motion period is used in the extrapolation scheme to evaluate critical capillary numbers Ca_{crit} demarcating squeezing from trapping. Due to Marangoni stresses, even light ($\beta = 0.05$) to moderate ($\beta = 0.1$) contaminations significantly reduce the average drop-phase migration velocity (compared to clean drops), especially at small $\lambda = 0.25$. In contrast, Ca_{crit} is weakly sensitive to contamination and levels off completely at $\beta = 0.05$. At $\lambda = 0.25$ and $c_{em} = 0.36$, the average drop-phase velocities are much different for lightly and moderately contaminated emulsions, except for near-critical squeezing when they become the same. Non-linear surfactant models (Langmuir, Frumkin) are used to validate the linear model.

EXAMPLE RESULTS

As one example of the physical trends², **Fig. 1** presents the snapshots from the Langmuir model simulation at three close time moments. The time moment t = 6.74 corresponds to the peak surfactant concentration $\Gamma = 3.9\Gamma_{ea}$ (i.e. $0.78\Gamma_{\infty}$) reached in the periodic cycle. The

linear model would be clearly inadequate for this Γ . However, such peak concentration in the Langmuir model simulation is observed only on a small portion of the drop surface, and only during a small portion t = 6.74 of the periodic cycle. Away from t = 6.74, the surfactant concentrations quickly fall to much smaller values on the entire surface, typical of the rest of the periodic regime. The deficiency of the linear model, therefore, does not have a global effect, and both models identically predict the integral flow properties, in particular, strong drop mobility reduction (2.8 times, on the average) due to surfactant.

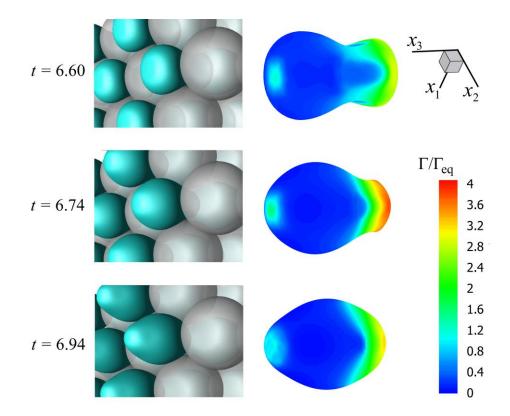


Figure 1: Snapshots of tight emulsion squeezing (left images) and surfactant concentration distribution (right images) for $\lambda = 0.25$, $c_{em} = 0.5$, $\beta = 0.1$ and $E = RT\Gamma_{\infty} / \sigma_0 = 0.5$.

REFERENCES

- Gissinger, J. R.; Zinchenko, A. Z.; Davis, R. H. Drops with insoluble surfactant squeezing through interparticle constrictions. J. Fluid Mech. 878, 324-355, 2019. <u>https://doi.org/10.1017/jfm.2019.678</u>.
- 2. Zinchenko, A. Z.; Gissinger, J. R.; Davis, R. H. Flow of a concentrated emulsion with surfactant through a periodic porous medium. *J. Fluid Mech.* **953**, A21, 2022. <u>https://doi.org/10.1017/jfm.2022.951</u>.